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HIGH PRESSURE POLYMORPHIC TRANSITIONS OF BISMUTH OBSERVED BY THE ULTRASONIC VELOCITY MEASUREMENT

By

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Abstract

Experimental method for determination of the ultrasonic velocity at very high pressure was studied. Single stage piston-cylinder apparatus was used as the high pressure chamber. Maximum pressure of 32 kb was attained easily without any trouble at room temperature. It is expected that this method will be available up to 40 kb combined with temperature of 1000°C.

High pressure polymorphism of bismuth which is accompanied with the abrupt change of the elastic wave velocity was examined. Shear wave velocity V_s was decreased extremely at the transition point Bi I-II, and increased again at Bi II-III, though the change of dilatational wave velocity V_p was almost negligible. It was shown that the velocity change of shear wave resembles remarkably with the electric resistance change.

Introduction

There have been always two important but opposed versions for the origin of the discontinuity or layered structure of the earth. Some authors explain that such discontinuous structures are caused by the change of chemical composition, but the others assert that these discontinuities arise from the phase change or chemical reaction retaining the main composition unchanged.

For instance, the origin of the Moho discontinuity has long been thought to be caused by the change of chemical composition from basic to ultrabasic. However, recent laboratory study for the phase diagrams of minerals showed that the above explanation is not the unique one but there is the possibility that such discontinuity is the result of basalt-eclogite (Kennedy G. C., 1956 ; Lovering T. F., 1958) or basalt-glaucophane schist transition (Newton R. C., G. C. Kennedy, 1963) retaining the chemical composition unchanged.

The origin of C layer is more complicated. Both theories, composition change and phase change, are samely reasonable to explain the nature of C layer. The phase diagrams for the silicate minerals at very high pressure and

temperature suggest that the possible minerals in C layer will be transformed into high pressure phase (Ringwood A. E., 1958 ; Sclar C. B. et al, 1962). On the other hand, it is hard to neglect that the transitional nature of this layer can be explained by the gradual change of chemical composition (Birch F., 1961).

Discontinuities and layered structures in the earth's interior were all discovered by the seismic wave velocities. The only observable values of the physical properties in the earth's interior are the elastic wave velocities (or the elastic constants). Accordingly, one of the most important methods to investigate the internal constitution of the earth is the direct measurement of elastic properties of minerals and various substances at high pressures and temperatures.

However, there are several difficulties to measure the elastic wave velocities at very high pressure and temperature corresponding to the sufficient depths of the earth's interior. These are: 1) ultrasonic transducer which can be used at sufficiently high temperature, 2) method observing ultrasonic velocity at very high pressure, 3) specimens which have low porosity and impurity, and also have the sufficient dimension (because, in some case, these specimens must be synthesized at high pressure and temperature).

In the present work, change of the elastic wave velocities which were accompanied by the polymorphic transition was studied for bismuth. Transition of bismuth is quite familiar and is also accompanied with remarkable change of volume and electric resistance (Bridgman P. W., 1949 ; Hall H. T., 1960).

Sudden decrease of electric resistance at transition suggest that there will be the substantial change of chemical bond. It has been reported that the electric conductivity is increased suddenly at C transitional layer (Rikitake T., 1950, 1951). There might be the close relation between the elastic wave velocity and electric conductivity at polymorphic transition.

Apparatus and Experimental Method

The single stage piston-cylinder apparatus was used as the high pressure chamber. Specimens were machined in cylindrical shape and placed in talc which acts as the pressure transmitting media. Schematic diagram of the apparatus is shown in Fig. 1. Details of this type of apparatus have been appeared in elsewhere (for instance, Kennedy G. C., P. N. La Mori, 1962) and will not be repeated in here. One of the lead wire was taken out from the center hole of the piston. Since the piston is the weakest part of the high pressure apparatus, the maximum pressure obtainable will be limited about 40 kb for the present apparatus. However, it will be easy to combine the

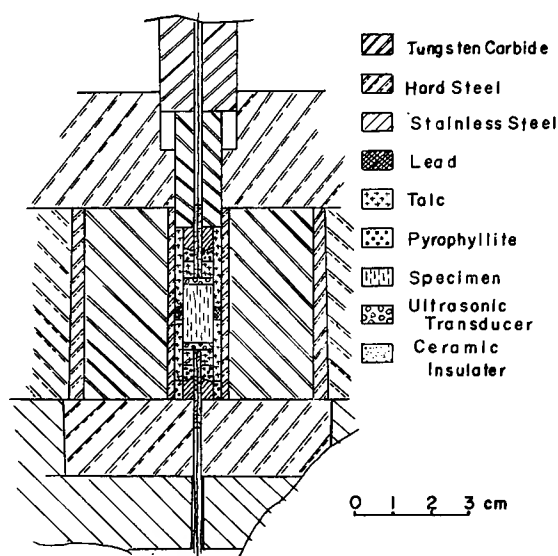


Fig. 1. Schematic diagram of the high pressure chamber for ultrasonic velocity measurement.

high temperature of 1000°C , placing the carbon heater in talc tube.

Maximum pressure reached was 32 kb for the present study. It covers the transition pressure of bismuth sufficiently. Bismuth ingot was crushed in fine powder and compressed and packed at 10 kb, then machined in cylindrical shape, about 15 mm long and 8 to 10 mm in diameter.

Barium titanate piezoelectric transducers were attached to the each end of bismuth specimen directly. Lead ring was putted on the specimen as the common electric ground. Time marker of the present ultrasonic instrument was 1, 2 and 10 MC, and the linearity of the synchroscope was quite excellent. The accuracy of the velocity was within 1 %.

Sensitivity of piezoelectric transducer was increased remarkably by the application of pressure. However, over 10 kb, the amplitude of the received waves was decreased rapidly with the increasing pressure. Above 20 kb, the piezoelectric efficiency of the transducer was lowered extremely and was not recovered again after the removal of pressure.

Transition was detected easily from the load vs piston-displacement diagram. The piston-displacement was measured by dial gage. It was observed that the transition was quite quick and almost instantaneous. However, sufficiently long time was spent to complete the transition.

After the few cycles of compression, the hysteresis curves of load vs displacement relation were coincided each other well. Then it was safely assumed

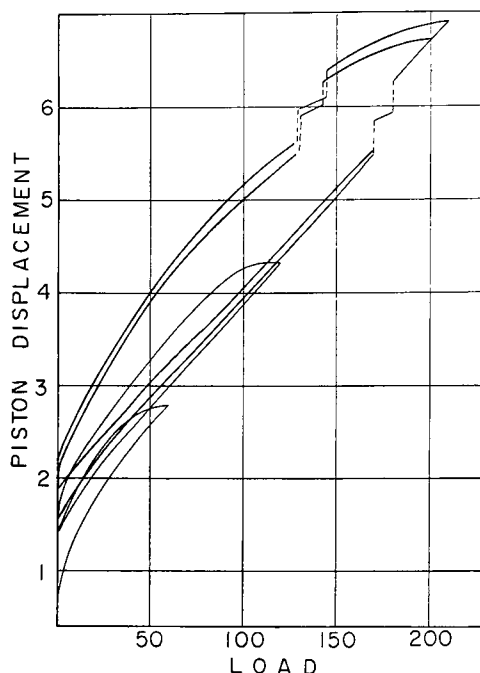


Fig. 2. Typical hysteresis curve of piston-displacement vs applied load.

that the deformation of the specimen was almost reversible and there was no further permanent flow. True pressure was estimated from the transition points Bi I-II and Bi II-III, it is 25.5 kb and 27.2 kb, respectively. Since the higher the maximum pressure reached, the more friction is remained in the pressure chamber on release of pressure, it was quite difficult to estimate the true pressure for unloading way.

The shortening of the specimen must be considerable at very high pressure, especially for soft substances. Unfortunately, the correction of shortening for velocity measurement was very difficult. The following three cases were assumed for the deformation of specimen embedded in solid material such as talc; 1) The compressibility of the specimen is same as the one for the surrounding medium, and the specimen is essentially plastic. For this case, $\Delta l/l_0$ will be equal $\Delta v/v_0$, since the compression of specimen is nearly one-dimensional. 2) The compressibility of the specimen is much smaller than the surrounding material and the specimen will behave approximately like rigid body. 3) The compressibility of specimen is extremely larger than that of the enclosing material, then the specimen will be compressed like the collapse of the balloon. For the later two cases, $\Delta l/l_0$ will be same as $1/3 \Delta v/v_0$. For the bismuth specimen embedded in talc, the first case was applied for increasing or

decreasing pressure, and the third case was used at the transitions. However, above correction is still just trial one, and must be checked again.

Results and Discussion

Fig. 3 and Fig. 4 show the variation of longitudinal and transverse wave velocities, V_p and V_s , with pressure up to 30 kb passing through the two transition points for bismuth polycrystalline specimens. At the transition pressure Bi I-II, both V_p and V_s were decreased. The decrement of V_p was quite slight, though it was more than the experimental error. On the other hand,

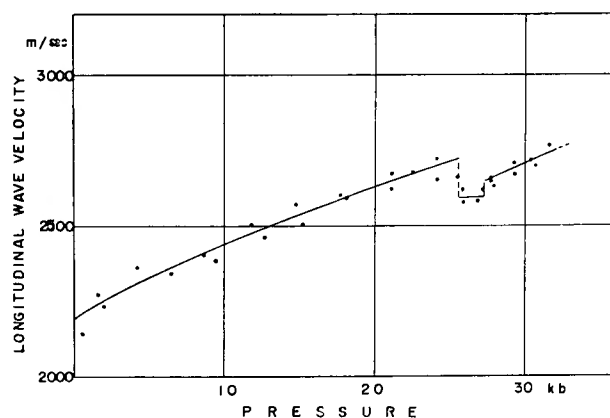


Fig. 3. Variation of the longitudinal elastic wave velocity V_p with pressure for bismuth.

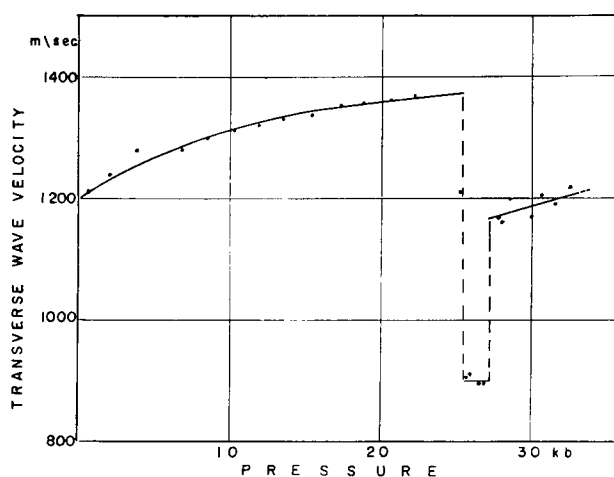


Fig. 4. Variation of the transverse elastic wave velocity V_s with pressure for bismuth. Abrupt velocity change corresponds to the transition Bi I-II and Bi II-III.

however, the decreament of V_s was quite remarkable. At the transition Bi II-III, V_p was increased slightly gain. V_s was also increased at Bi II-III, but the value was much lower than the V_s of Bi I.

The behavior of V_s at the transition points resembles quite well with the electric resistance, which is shown in Fig. 5 (after Hall H. T., 1960). The abrupt change of V_s means the abrupt change of rigidity μ . Then it well be supposed that there is the close connection between the electrical conductivity and rigidity at the transition. Sudden decrease of electric resistance at Bi I-II might be caused by the change of some degree of the chemical bond.

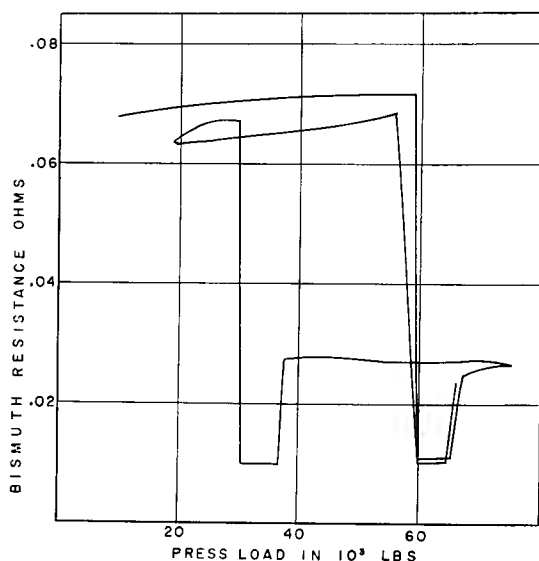


Fig. 5. Variation of the electrical resistance with pressure for bismuth. (After H. T. Hall, 1960).

For the comparison with the static measurement of compressibility, the value $\phi = V_p^2 - 4/3 V_s^2$ was calculated. For isotropic homogeneous substances, ϕ corresponds k_s/ρ . k_s/ρ and μ/ρ are the only observable values of the physical properties in the earth's interior. Usually the difference between k_s and k_T (adiabatic and isothermal bulk modulus) is negligibly small. Fig. 6 shows the $P-\phi$ and $P-k_T/\rho$ relations for bismuth. The coincidence between ϕ and k_T/ρ was not so good. Though the coincidence at low pressure was fairly well, but it became worse at higher pressure. The poor agreement will arise from the following reasons, that is, the grain size was not so fine enough comparing to the wave length and so the isotropic and homogeneous assumptions could not be applied, or there might be any kind of substantial technical

error for the determination of wave velocities. This discrepancy was the most troubled problem for determination of elastic wave velocity at very high pressure.

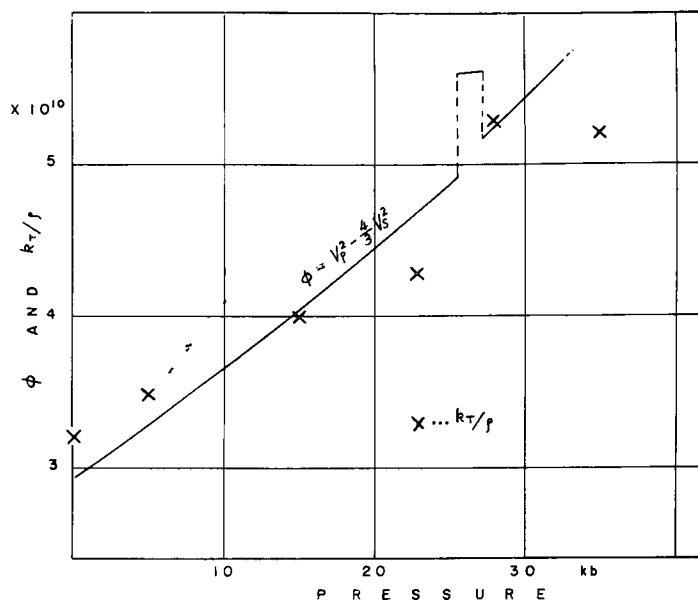


Fig. 6. $P \sim \phi = V_p^2 - 4/3 V_s^2$ and $P \sim k_T/\rho$ relations for bismuth.

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